THE EFFECT OF FLOW CONDITIONS ON CATALYTIC YIELDS

BY

THOMAS BARON

B. S., University of Illinois, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING
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Introduction

Heterogeneous reactions are usually carried out in packed beds. From the experimental point of view the use of such equipment produces some obvious difficulties. The interpretation and generalization of results are complicated by uncertainties regarding flow conditions, temperature and concentration distribution, and time of contact. Furthermore, due to the irregular pattern formed by the catalyst surface, exact mathematical treatment of mass and heat transfer in the bed becomes impossible.

For the present investigation the apparatus was designed to obviate some of these difficulties. The oxidation of sulfur dioxide, catalyzed by vanadium oxide, was carried out in a tubular reactor, and data were taken with the purpose of studying the effects of temperature, time of contact, and concentration of reactants on conversion. On the basis of this investigation and previous work, a comparatively simple theory was developed by means of which it is possible to explain adequately the experimental results obtained.

In order to account for the surprising effect of inert gasses on the activation energy of the reaction, the collision theory was extended to describe the mechanism of catalytic activation by collisions. In addition this work contains an extension of the theory of tubular reactors to first order reversible reactions, a statistical theory of mass and heat transfer in packed beds, and a simplified mathematical theory for the description of first order consecutive reactions.

Theoretical

Results of experiments performed by Manning[1] on the catalytic oxidation of sulfur dioxide in an apparatus

similar to that used in the present work show a surprising influence of the nature of the inert gas on the activation energy of the reaction. A theory was developed as part of the present work to explain these results. The number of collisions between adsorbed molecules to be activated and molecules from the gas phase is multiplied by the probability of an energy exchange sufficient to activate the adsorbed molecules. By comparing the resulting equation, which gives the rate of activation by collision, with the Arrhenius equation it is shown that for the desorption of product molecules

$$E_a = (1+r)^2 E/4 \qquad (1)$$

The above considerations, when applied to a modification of Bodenstein's[2] diffusion theory, yield the following equation expressing the apparent activation energy of the catalytic oxidation of sulfur dioxide as a function of the activation energy of desorption of sulfur trioxide and the ratio of the molecular weight of the gases above the catalyst:

$$E_a = [2/3 + (1+r)^2/12]E \qquad (2)$$

Damkohler's[3] theory for heterogeneous reactions in tubular reactors is extended to cover the case of first order reversible reactions. It is shown that these equations can be used to estimate the relative importance of the resistances introduced by mass transfer and reaction.

For the statistical theory of mass and heat transfer in packed beds the equations of Lerman[4] are used to obtain the concentration profiles in packed beds. Comparing this equation to the solution of the differential equation for mass transfer, the following expression is found for the effective diffusivity in packed beds:

$$D = KVd \qquad (3)$$

From the analogy between the processes of mass and heat

transfer, the equation for the effective thermal conductivity in the bed is

$$k = KcGd \qquad (4)$$

Integration of the rate equation for simple reactions presents no difficulties. However, for systems in which several consecutive and side reactions occur, the rate equations can be integrated only by tedious methods. The methods of matrix calculus, however, can be used to advantage. A general formula is derived which is applicable to any first order reaction system. This formula contains a matrix whose elements are composed of the specific reaction rate constants of the reactions involved. Rules are given for the construction of this matrix.

Experimental

The catalyst tube was a cylindrical tube of Refractory Alundum, ¼-inch i.d., ½-inch o.d., and 24 inches long carrying potassium meta-vanadate, amounting to 7.4% of the total weight of the catalyst tube. The tube was housed in a brass billet 2-½ inches o.d., ¾ inches i.d., and 26 inches long. The inside temperature of this billet was measured by thermocouples placed into wells drilled into the brass.

Results and Conclusions

The results are presented in tabular and graphical forms for the isothermal oxidation of sulfur dioxide. The data are analyzed with the aid of the theories developed in the theoretical section. The following conclusions are reached:

1. The diffusional resistance in the oxidation of SO_2 is less than 5 percent of the overall reaction resistance for the conditions investigated.

2. The oxidation of SO_2 catalyzed by vanadium oxide is a reaction of the first order in the SO_2 concentration,

and one-half order in the oxygen concentration. The reverse reaction in first order in the concentration of SO_3. The retarding effect of SO_3 depends on the ratio of the rate of reaction to the rate of adsorption of SO_3.

3. The apparent activation energy of the reaction is a function of the activation energy of desorption for SO_3 and the ratio of the average molecular weight of the gases above the catalyst to the molecular weight of SO_3.

4. The tubular reactor is particularly well suited for fundamental investigations in heterogeneous reaction kinetics. Its chief advantages are: ease of temperature control, exactness of mathematical treatment, and good reproducibility of results.

Nomenclature

c = specific heat
D = effective diffusivity
d = effective diameter of packing
E = activation energy of desorption
Ea = apparent activation energy
G = mass velocity
k=Thermal conductivity
K = constant, property of the packing
r = ratio of the molecular weight of product and molecular weight of gases above catalyst
V = velocity of fluids, based on empty bed

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VITA

The author was born in Budapest, Hungary on February 15, 1921. He attended the public schools of that city, and graduated from Verboeczy Gymnasium. He entered the United States in 1939, and enrolled in De Paul University in the fall of that year. In the fall of 1940 he transferred to the University of Illinois, where he received the Degree of Bachelor of Science in Chemical Engineering in June, 1943. He held the position of Assistant Engineer with National Varnished Products Corporation, Rahway, New Jersey, from June, 1943 to February, 1944, at which time he entered the army. He became an American citizen in June, 1944, and after having served in the American Theater of Operations for a period of two years, he was honorably discharged. In February, 1946 he entered the Graduate School of the University of Illinois, where he held successively the positions of Graduate Assistant in Chemistry, Graduate Research Assistant in Chemical Engineering, and Graduate Fellow in Chemical Engineering.

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